

# ENCYCLOPEDIA OF POLYMER SCIENCE AND ENGINEERING

## VOLUME 4

Composites, Fabrication  
to  
Die Design

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A WILEY-INTERSCIENCE PUBLICATION

John Wiley & Sons

NEW YORK • CHICHESTER • BRISBANE • TORONTO • SINGAPORE

**Photodegradation.** PMMA is very resistant to solar uv; it essentially does not absorb at  $\geq 300$  nm and absorbs only weakly at 273 and 288 nm (131). However, because of its use as protective cover plates for solar collectors, PMMA photodegradation has been studied over very long exposure time (132). The presence of methyl methacrylate monomer accelerates PMMA photooxidation and a singlet oxygen mechanism has been implicated (eq. 63) (133).



However, although the drop in PMMA molecular weight during photooxidation is proportional to the initial monomer content, the monomer level reaches a plateau after a few thousand hours of xenon-arc irradiation. The high stability of PMMA to free-radical oxidation (eqs. 22-26) compared with PE, for example, may result from the  $-\text{CH}_3$  groups' inaccessibility to peroxy radicals because of steric crowding, so that only  $\text{CH}_2$  sites are available for attack. From Table 4, primary CH sites are about ten times less reactive than  $\text{sec-CH}$  groups to peroxy radical attack.

Once a terminal radical is formed, PMMA unzips thermally to reform monomer (eq. 64; see also eq. 21). This process can be suppressed in PMMA by the presence of comonomers.

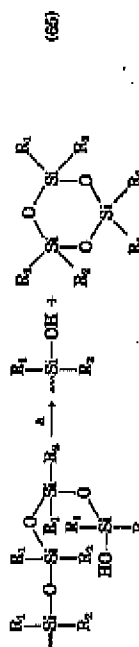


The *tert*-radical has been identified by esr from both vacuum- and air-irradiated polymer (131). During long wavelength irradiation, both random scission and unzipping occur; unzipping becomes more important as wavelength increases.

#### Polysiloxanes

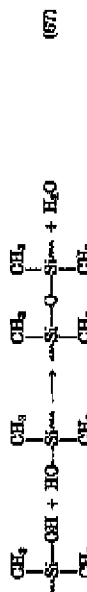
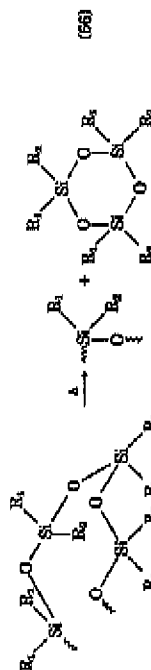
These polymers are frequently used as rubbery sealants, adhesives, or coatings where extreme resistance to weathering or high temperatures is required. They are attacked slowly under prolonged or extreme hydrolysis conditions.

**Thermal Degradation.** The high temperature stability of polysiloxanes has led to their use as high temperature sealants. Their stability is influenced by the polymerization conditions, impurities, and end-capping (134,135). Above ca 350°C, oligomer elimination from chain ends occurs (eq. 65).



Where  $\text{R}_1, \text{R}_2 = \text{CH}_3$  or  $\text{C}_6\text{H}_5$

If the end groups are blocked, a slower oligomer elimination from the chain center can occur (eq. 66). At temperatures below 300°C, for unblocked polydimethylsiloxane, chain coupling occurs (eq. 67).



Phenyl substituents enhance thermal stability, in part through branch or cross-link formation. Free-OH end groups actually enhance the thermal stability of phenyl-substituted polymers by promoting the branching reaction (eq. 68) (135).



The thermal stability of siloxanes with phenylene groups in the backbone, such as poly(tetramethyl-*p*-silylphenylene) siloxane, has been studied (136).

**Hydrolysis.** Siloxanes undergo an acid- and a base-catalyzed depolymerization (eq. 69) (22,137), so that it is important to eliminate the acid or base catalysts used in their polymerization.



#### Cellulose

As an abundant natural product, cellulose is used in many forms, the most visible being fibers and films. Depending on the presence of impurities or dyes, cellulose may be very sensitive to weathering, heat, and solutions of acids, alkalis, or oxidizing agents.

**Photooxidation.** Cellulose is seldom found pure, but rather it is contaminated with traces of wax or tannin residues, both of which absorb uv and sensitize the degradation of cellulose. Cellulose itself should not absorb above 280 nm, but usually has a weak absorption at ca 285 nm. This is attributed to the acetal (glycosidic) group in cellulose (138). However, it is more likely due to carbonyl or transition-metal impurities (139). It is not due to an  $\text{O}_2$ -charge-transfer complex with cellulose (139).

Irradiation of cellulose in the solar region leads to a mixture of oxidation products including ketones, aldehydes, acids, and hydroperoxides; peroxy radicals are detected by esr (139). Radical yields are higher at higher absorbed mois-